

Enabling Science for Advanced Ceramic Membrane Electrolyzers

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Introduction

Efficient and economical electrolysis of water to hydrogen and oxygen gases is of great importance to renewable hydrogen energy programs. Combined fuel cell/electrolyzer systems offer the potential for efficient energy storage and conversion. Unfortunately, low-cost and low-maintenance electrolyzer technologies are not commercially available. Current alkaline and polymer membrane based electrolysis systems suffer from the following disadvantages:

- The hydrogen product gas is saturated with water vapor; the gas must be dried before the hydrogen can be stored in a hydride bed.
- Both technologies require high loadings of precious metal catalysts to reduce the overpotential losses.
- Neither technology is amenable to high-pressure operation. It is very difficult to pressurize wet alkaline electrolyte cells. Polymer membrane cells allow high crossover rates of gases across the membranes at elevated pressures.
- Long-term stability and contamination is a problem with both alkaline and PEM electrolysis electrolytes. Alkaline electrolytes adsorb carbon dioxide readily and form carbonates. Polymer membrane systems must use very pure de-ionized water or they will accumulate cations that displace protons and increase the cell resistance over time.

A promising alternative to liquid and polymer membrane electrolytes is a proton conducting ceramic solid electrolyte technology. This technology is intrinsically different than zirconia-based oxygen ion electrolyzers in that the transported (separated) species is hydrogen rather than oxygen. The zirconia oxide ion systems produce a wet hydrogen product stream. The proton conducting ceramic electrolyte does not suffer from this disadvantage and produces a hydrogen stream with no further purification needed. The electrolysis of water vapor on oxygen ion and proton conducting ceramics is illustrated in Figure 1. Other advantages include possibly better electrode kinetics and reduced I.R. losses. We propose to demonstrate the feasibility of water electrolysis using solid-state electrochemical cells based on proton ion conducting solid electrolytes. The ceramic materials transport protons through a crystalline lattice. These materials offer a number of potential advantages over current systems.

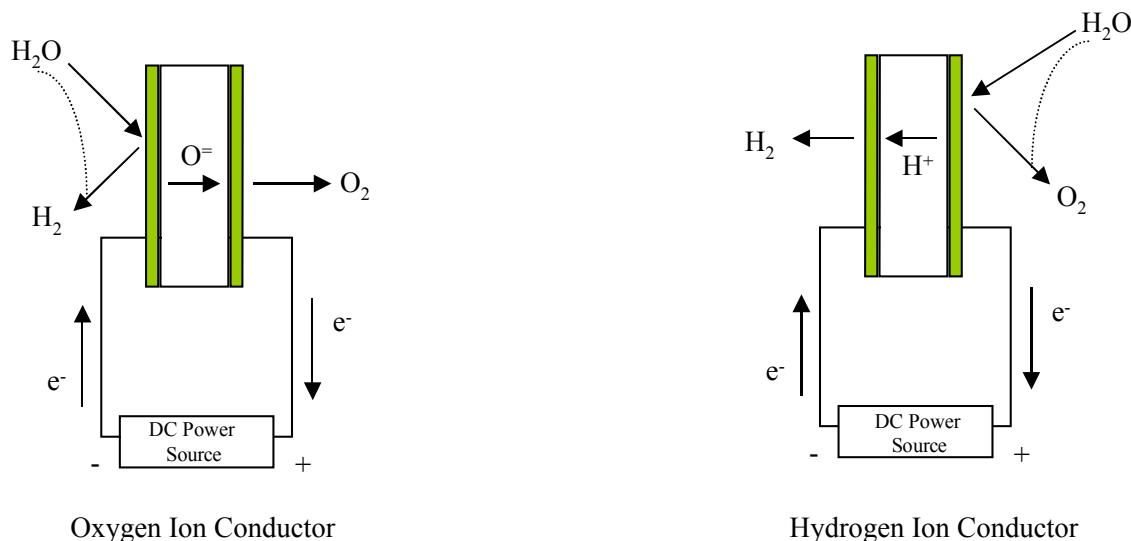


Figure 1. Schematic illustration of water electrolysis on a oxygen ion conducting electrolyte (right) and a hydrogen ion conducting electrolyte (left)

The ceramic electrolyzers are solid-state devices with no polymer or liquid electrolyte to contaminate and they are well suited to operate at elevated pressures. The devices should operate with steam without expensive cation removal/carbon dioxide pretreatment. The ceramic cells operate at temperatures from 450-800°C and thus at a lower thermodynamic potential than the low-temperature systems. The elevated operating temperatures enable the use of non-precious metal electrodes, and electrode reaction kinetics may also be faster at these elevated temperatures. Temperatures in this range are directly compatible with solar furnace operating temperatures, offering potentially attractive integrated hybrid electrical/hydrogen generation systems. Finally the materials transport protons without water and thus produce a dry hydrogen electrolysis product.

Background

Recently, a number of perovskite structure ceramic proton separation membranes have been developed been reported by Iwahara et. al. [1]. These materials exhibit good stability, high ionic transport rates for protons and also operate in the 600-900°C temperature range which is optimal for *insitu* catalysis reactions. The materials are also of great value for high temperature fuel cell technologies, isotope separation systems, sensor applications and heterogeneous catalysis.

The proton conducting materials are rare earth cerate and zirconate ABO_3 formula oxides e.g. $(\text{Sr},\text{Ba})(\text{Zr},\text{Ce})(\text{B})^{3+}\text{O}_{3-y}$ where $(\text{B})^{3+}$ is a three valent yttrium or lanthanide cation. The crystal structures of all of these materials are typically orthorhombic distortions of the cubic perovskite structure due to a tilt of the oxygen coordination octahedra as illustrated in Figure 2. The perovskite materials contain oxygen ion vacancies introduced by the $(\text{B})^{3+}$ substituting for four valent zirconium or cerium. Exposing these materials to steam at elevated temperatures causes water to hydrolyze and fills the vacancies with oxygen and two mobile protons.

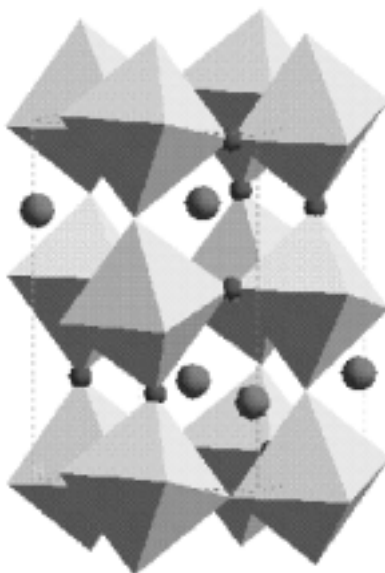


Figure 2. Polyhedral representation of the $(\text{Sr,Ba})(\text{Zr,Ce})(\text{B})^{3+}\text{O}_{3-y}$ perovskites where $(\text{B})^{3+}$ designates a trivalent substituted cation. The (Sr,Ba) occupy the A site, $(\text{Zr,Ce})(\text{B})^{3+}$ occupy the B center positions of the octahedrally coordinated oxygen.

Since these first reports, Iwahara and other investigators have studied the conductivities (both ionic and electronic), conduction mechanism, deuterium isotope effect, and thermodynamic stability of these materials. The motivation for most of this work derives from the desire to utilize these materials for high temperature, hydrogen-fueled solid oxide fuel cells. In a reverse operation mode, if metal or metal oxide electrodes are deposited onto a dense pellet of this material and is heated to temperature T , the application of an electric potential to the electrodes will cause a hydrogen partial pressure difference across the pellet according to the Nernst equation:

$$\Delta V = -\frac{RT}{zF} \ln \frac{P'_{H_2}}{P_{H_2}}$$

where F is Faraday's constant and z is the number of electrons transferred upon oxidation and reduction. For example, at 500°C the application of 1.5V would produce a hydrogen partial pressure difference across a pellet on the order of 10^{20} . These differences in hydrogen activity are high enough to decompose water at elevated temperatures.

The Sr and Ba-doped cerate electrolytes exhibit the highest proton conductivities, however, recent reports question the thermodynamic stabilities of the Ba compounds at intermediate temperatures and in the presence of high partial pressures of CO_2 and H_2O . It is unclear whether this will present a problem for electrolysis applications; therefore, we will evaluate the thermodynamic stability of these materials and study the stability of potential substitute candidates. Ceramics processing also plays an important role in determining the conductivities of these materials. Figure 3 displays the conductivities of three $\text{Sr}_{0.95}\text{Yb}_{0.05}\text{CeO}_{3-x}$ samples made using differing starting powders and sintering schedules.

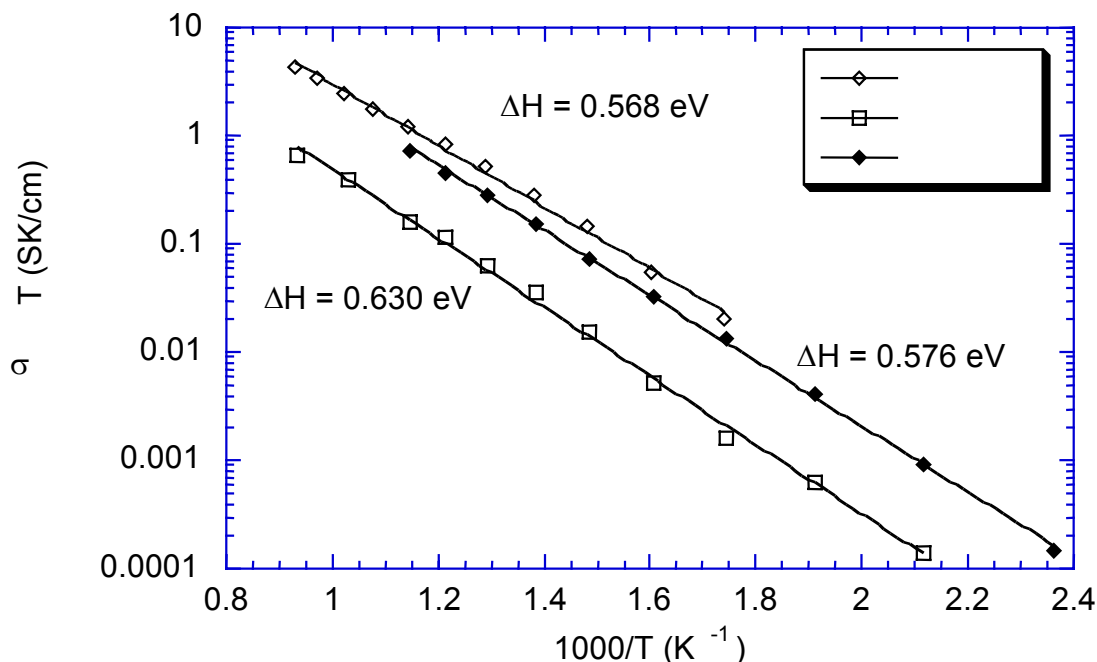


Figure 3. The conductivities of three $\text{Sr}_{0.95}\text{Yb}_{0.05}\text{CeO}_{3-x}$ ceramic samples produced using differing ceramic processing methods.

Objectives

The principal goal of this project is to demonstrate electrolysis technology using ceramic electrochemical cells based on solid oxide proton conductors. Los Alamos has experience in solid-state bulk and thin film materials synthesis and characterization capability. We will synthesize and characterize electrolyte and electrode materials and fabricate test cell apparatus. Characterization methods available in the Electronic and Electrochemical Materials and Devices Group include XRD, TGA, EDAX, SEM and AC impedance and DC cyclic voltammetry electrochemical methods.

- Evaluate proton-exchange ceramic membranes for use in electrolyzers
- Fabricate dense ceramics of cerates and zirconates and measure the bulk hydrogen conductivity using AC impedance spectroscopy and DC conductivity measurements, demonstrate water electrolysis using these materials
- Synthesize electrode materials for electrolysis and characterize their polarization behavior using electrochemical methods

Current Progress

The funding for this new project was received only three months before the 2002 Hydrogen Program Annual Review. Consequently, we are in the startup phase of our program. Our first task was to identify candidate perovskite oxide materials with high protonic conductivities. We have identified yttrium doped strontium cerate and yttrium doped strontium zirconate materials as possible electrolyte materials. Barium cerate perovskites exhibit higher protonic conductivity but the reactivity with carbon dioxide would require pretreatment of the steam.

We have designed and assembled a high temperature AC impedance system for measurement of protonic conductivities. Our measurements of candidate ceramic protonic conductivities indicate that the electrolyte resistance in thick membrane form should not impose a large I.R. loss on the electrolysis cell.

We have identified and contracted a ceramics supplier, TYK Corp, to fabricate electrolyte tubes for prototype electrolyzer research studies. The supplier has successfully manufactured and delivered closed end electrolyzer membrane tubes to LANL. The composition of the tubes is $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$. Figure 4 is a photograph of a recently manufactured electrolyzer tube.



Figure 4. Ceramic electrolyte tube of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ custom fabricated for LANL by TYK Corp.

References

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